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The Measurement of Hydrocarbon Emissions from Fugitive Sources in Petroleum Refineries

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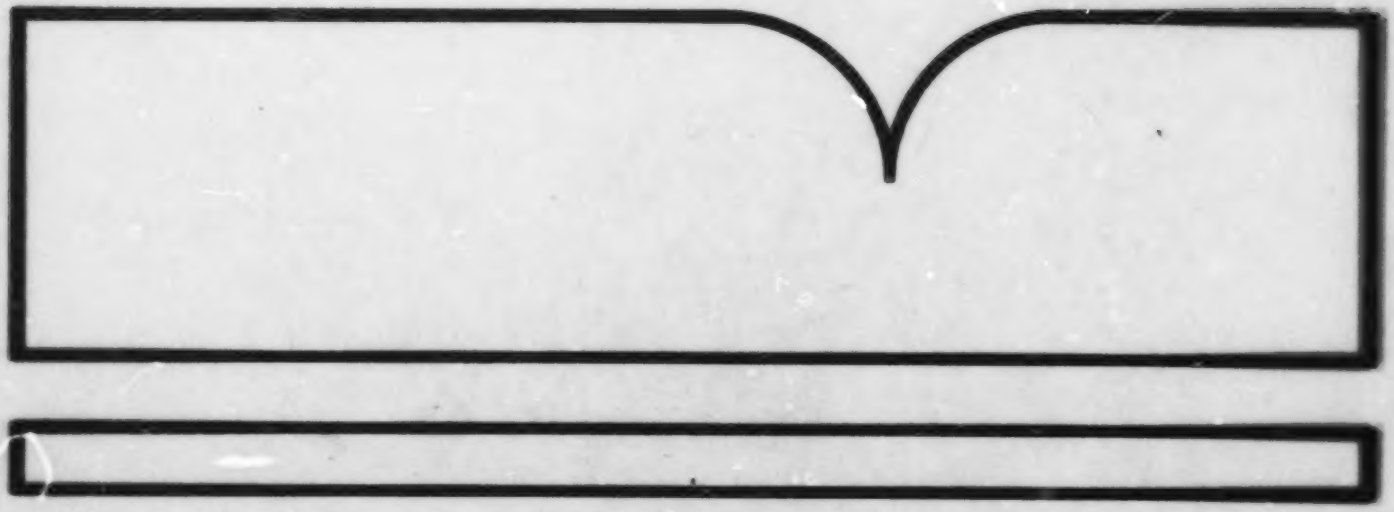

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16. ABSTRACT
The paper gives preliminary results of measurements of hydrocarbon emissions from a number of petroleum refineries. Sampled sources included valves, flanges, pump and compressor seals, pressure relief devices, drains, and cooling towers. The paper discusses sampling techniques and describes the analyses and correlation of the sampling data. Data obtained to date supported the following conclusions: (1) Emissions from flanges are not significant. (2) Compressor seals have the highest average leak rate of the baggable sources. (3) Valves contribute more emissions than any other single baggable source. (4) Most leakage occurs from a relatively few sources of each source type. (5) The type of process stream has a substantial effect on the source emissions. (6) Losses from cooling towers are quite low.

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THE MEASUREMENT OF HYDROCARBON EMISSIONS FROM FUGITIVE SOURCES IN PETROLEUM REFINERIES

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and
Atly Jefcoat

Measurement of hydrocarbon emissions from fugitive sources are being made at a number of refineries. Sampled sources include valves, flanges, pump seals, compressor seals, pressure relief devices, drains, and cooling towers.

The sampling techniques are presented and discussed. The analyses and correlation of the sampling data are described. Preliminary results are given.

INTRODUCTION

The petroleum refining industry is a significant source of atmospheric hydrocarbon emissions in the United States. The hydrocarbon emissions from refineries and associated industries play a significant role in air quality problems, particularly with oxidants.

Two types of hydrocarbon emissions can be defined, controlled and uncontrolled. Controlled emissions issue from stacks or vents, and they can be readily identified and quantified. Uncontrolled or fugitive emissions result from leaks which may occur in almost any hydrocarbon service. Fugitive leaks require specialized techniques for measurement.

The program described in this paper is being sponsored by the Environmental Protection Agency (EPA). The completed program will provide a data base for:

a) Estimation of the environmental impact of existing and new refineries (including health effects),

b) Definition of the status of control technology and needs for development of additional controls, and

c) Development of emission factors that are suitable for use in permitting and off-set analyses in non-attainment areas.

SOURCE DESCRIPTION

Fugitive emissions are released to the atmosphere primarily from leaks and open surfaces. They escape without control of rate, direction, or composition. Hydrocarbon emissions from fugitive sources in refineries were studied in 1958 (1). There has recently been renewed interest in emissions from these sources (2, 3, 4).

There are many such sources within petroleum refineries. For convenience in this study, these sources have been classified into two principal groups, baggable sources and non-baggable sources. Those sources which cannot be practically enclosed to measure losses are classified as nonbaggable sources. Included in this category are sumps, cooling towers, some process vents and the various units of the wastewater treating system.

Baggable sources are those that can be completely enclosed to measure their emission rates. The emissions from six types of baggable sources; valves, flanges, pump seals, compressor seals, pressure relief

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valves, and drains are discussed in this paper. In addition, the emissions from cooling towers are discussed. These results are based on sampling at nine refineries. The results are preliminary and are subject to revision at the conclusion of the program.

SOURCE SELECTION

By sampling in 12 to 14 refineries throughout the country, a wide variety of process units, crude oils, and process equipment will be included in the completed study. In each refinery, sources in seven to nine different process units are selected for sampling.

Baggable source variables which might affect the fugitive emission rates are classified as either choice or correlating parameters. A choice parameter is one which is felt to directly affect fugitive emissions and is used in defining the distribution of those sources selected for sampling. The choice parameters for two baggable sources are listed in Table 1.

All other variables which are considered to have some potential for affecting leak rates are classified as correlating parameters. The number of correlating parameters ranges from 17 for pumps to two for drains.

There are normally 500 to 600 sources studied in each refinery. Individual sources are selected for sampling from piping, instrumentation, and process flow diagrams. An unbiased, random selection of sources can be achieved with this procedure.

EXPERIMENTAL PROCEDURES

Source Screening

Each selected baggable source is screened with a sensitive hydrocarbon detector. Either the J. W. Bacharach Instrument Company "TLV Sniffer" or the Century Instruments Organic Vapor Analyzer (Model OVA-108) are used. Both instruments are calibrated with standard mixtures of n-hexane in air.

When screening valves, pumps or compressors, the probe of the hydrocarbon detector is placed as close as possible to the intersection of the shaft with the sealing device. The probe is held at each location for a minimum of five seconds. The detector reading is recorded. This is repeated at four points 90 deg. apart around the shaft. The maximum reading is used as the sampling criterion.

Flanges are screened by placing the detector probe at 2-in. intervals all around and right against the outside perimeter of the flange interface. The maximum detector reading is recorded. Drains are similarly screened. The detector probe is placed at 2-in. intervals around the perimeter of the drain. The maximum measured hydrocarbon concentration is recorded.

Pressure relief valves are only screened if they vent directly to the atmosphere. The detector probe is placed at the midpoint of the vent or "horn" outlet to obtain the screening value.

A hydrocarbon vapor leak rate of 150 cc./hr. or less from any single baggable source is considered negligible and the source is not sampled. It has been found that hydrocarbon detector readings below 200 p.p.m. around a baggable source generally indicate a leak rate of less than 150 cc./hr.

Baggable Source Sampling

The preferred method for measuring the hydrocarbon leak rate from baggable sources is the dilution method. The sampling train used with this procedure is shown in Figure 1.

Mylar® plastic (polyethylene terephthalate) is used to enclose the leaking sources. Mylar® does not significantly adsorb hydrocarbons, it is very strong, and it has a high melting point (250°C.). Each enclosure is kept as small as practical.

A cold trap is placed in the system to condense water and heavy hydrocarbons. This prevents condensation in downstream lines and equipment. Any organic condensate that collects in the cold trap is measured and included as part of the hydrocarbon leakage.

A slight vacuum is maintained inside the enclosure at all times. This insures that there will be no loss of air and hydrocarbon vapor to the atmosphere.

A gas flow rate of two to four cu. ft./min. is maintained through the sampling train during sampling.

When equilibrium has been reached, samples of the gas passing through the train are collected in Tedlar plastic bags. At the same time, samples of ambient air around the measured source are collected. Just before taking these samples, the gas pressure,

temperature, and flow rate and barometric pressure are recorded.

The total methane and nonmethane contents of the gas samples are determined with a Byron Instrument Model 301 C Total Hydrocarbon Analyzer (THC). The THC uses a flame ionization detector for the measurement of hydrocarbon concentrations. Nonmethane hydrocarbons are assumed to be hexane for calculational purposes.

Controlled laboratory testing has shown that the hydrocarbon leak rate can be calculated from the gas flow rate and hydrocarbon content.

Cooling Tower Sampling

From one to six cooling towers are sampled at a refinery. Inlet and outlet water samples are collected at intervals during each day of a five-day test period. Composites of daily samples are purged with nitrogen to determine the volatile hydrocarbon content of both the inlet and outlet water streams. The purge gas rate is measured and the gas is collected in a Teflon bag. After the purging operation, the collected gas is analyzed for hydrocarbons with the THC.

The cooling tower emissions are estimated from the difference in the volatile hydrocarbon content of the inlet and outlet water samples.

Results

Preliminary sampling data from nine refineries have been used to develop the results presented in this paper. It should be emphasized that these results are subject to revision as the program continues.

Baggable Sources - Screening

Sources in all the major types of refinery processing units were screened. The distribution of the baggable sources screened in the various process units are shown in Table 2. Over 5,600 baggable sources were sampled. More valves were sampled than any other source.

The maximum screening value, expressed as p.p.m.v. hexane, was used as the sampling criteria. The distributions of the maximum screening values are shown in Table 3 for valves and pump seals. These distributions are typical of those seen for the other baggable sources. The majority of the leakage occurs from the few sources that give the higher screening values. In the case of valves, for example, only about 10% of the total screened valves have screening values above 10,000 p.p.m.v. Yet, these valves are responsible for over 70% of the total leakage.

Over 80% of the emissions from pump seals are lost from those seals which screen above 10,000 p.p.m.v. This same trend holds true for flanges, compressor seals, drains, and pressure relief devices. The fraction of these sources screening above 200 p.p.m.v. as hexane are shown in Table 4.

Several types of screening values were investigated to develop correlations with source leak rates. One such correlation is shown for valves in Figure 2. In this figure, the $\log_{10}$ of the sum of the average stem and average gland screening value is shown as a function of the $\log_{10}$ of the total leak rate (lb./hr.). The relationship is quite good with a correlation coefficient of about 0.8. These types of correlations can be used to estimate leak rates from the screening values.

For valve monitoring programs, the maximum screening value is simpler to obtain than average screening values. Correlations of valve leak rates as a function of the maximum screening value (p.p.m.v. as hexane) have been developed. Nomographs based on these correlations are presented in Figures 3 and 4. These nomographs can be used to predict valve leak rates. All screening values were obtained with a J. W. Bacharach "TLV Sniffer" calibrated with n-hexane.

Baggable Sources - Sampling

From preliminary data, compressor seals were found to have the highest emission factor of the six baggable source types. The emission factor for flanges is, by far, the lowest. Even though there are a large number of flanges in a refinery, their total contribution to refinery emissions is small.

Of the six baggable source types, valves are the largest contributor of refinery hydrocarbon emissions. This is because of their relatively large number and their significant emissions.

The effect of process stream types on emission rates was investigated. Each process stream was classified into one of three basic stream groupings. These groups are gas/vapor streams, light liquids/two-phase streams, and

heavy liquid (kerosene and heavier) streams. The emission factors were determined for sources in each group. The normalized factors are presented in Table 5 for valves and pumps. The stream type apparently has a considerable effect on the emission factors for pumps and valves. Emissions from valves in gas service are almost two orders of magnitude greater than those from valves in heavy liquid service. This same trend, although not quite so pronounced, is evident in pump seal emission factors.

Nonbaggable Sampling - Cooling Towers

Thirty-one cooling towers were sampled to determine the loss of volatile hydrocarbons to the atmosphere. Six of the 31 towers had measureable emissions. The average emission factor for cooling towers is quite low. They do not represent a substantial source of hydrocarbon emissions from refineries.

CONCLUSIONS

The data obtained thus far in this study support the following conclusions:

1. Emissions from flanges are not significant.
2. Compressor seals have the highest average leak rate of the baggable sources.
3. Valves contribute more emissions than any other single baggable source.
4. The majority of the leakage occurs from a relatively few sources of each source type.
5. The type of process stream has a substantial effect on the source emissions.
6. Losses from cooling towers are quite low.

ACKNOWLEDGEMENT

The work described in this paper was conducted for the U.S. Environmental Protection Agency under Contract No. 68-02-2147 (Exhibit B) and 68-02-2665. The contributions of Sheryl Preston, C.D. Smith, and the entire Radian program staff are gratefully acknowledged.

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2. Report Number 911-115-1661, Meterology Research, Inc. (1976).
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4. Publication Number 4262, American Petroleum Institute (1975).

TABLE 1. RANGE OF CHOICE VARIABLES FOR SCREENED VALVES AND PUMP SEALS

Baggable Source	Choice Variable	Variable Ranges for Screened Sources
Valves	Pressure	0 to 1600 lb./sq. in. gauge
	Temperature	-30 to 925°F.
	Fluid State	Gas, Liquid
	Service	In-Line, Open-Ended
	Function	Block, Throttling, Control
	Size	0.5 to 24 in.
Pump Seals	Pressure	0 to 2000 lb./sq. in. gauge
	Temperature	-30 to 740°F.
	Capacity	5 to 600 g.p.m.
	Shaft Motion	Centrifugal, Reciprocating
	Seal Type	Mechanical, Packed, Double, Single
	Liquid RVP	<1.5, 1.5 to 10.5, >10.5 lb./sq. in. gauge

TABLE 2. DISTRIBUTION OF SCREENED SOURCES IN REFINERY PROCESS UNITS

	Number of Individual Sources					
	Valves	Flanges	Pump Seals	Compressor Seals	Relief Valves	Drains
Atmospheric Distillation	278	414	153	6	14	21
Vacuum Distillation	57	78	25	-	1	2
Hydrotreating/Hydrorefining	286	247	61	14	7	27
Catalytic Cracking	190	253	77	31	15	17
Catalytic Reforming	142	264	41	32	7	21
Hydrocracking	83	33	40	10	-	12
Alkylation	227	270	76	10	19	34
Light Ends/Gas Processing	460	148	153	45	28	57
Sulfur Recovery	10	6	-	-	-	3
Dewaxing/Treating	289	300	65	5	-	27
Hydrogen Production	49	19	7	-	2	8
Delayed Coking	86	32	37	16	4	11
Hydrodealkylation	36	15	5	2	-	5
Aromatics Extraction	45	15	43	3	4	7
Other	11	6	10	1	-	2
	2249	2100	793	175	101	254

TABLE 3. DISTRIBUTION OF MAXIMUM SCREENING VALUES

Screening Values Range, p.p.m.v. Hydrocarbon[b]	Screened Sources Within Range	
	Number	Percent
Valves		
Missing[a]	31	1.4
0	1110	49.3
1 to 200	524	23.3
201 to 1000	140	6.2
1001 to 10000	231	10.3
>10000	213	9.5
	2249	100%
Pump Seals		
Missing[a]	46	5.8
0	168	21.2
1 to 200	228	28.8
201 to 1000	100	12.6
1001 to 10000	131	16.5
>10000	120	15.1
	793	100%

[a]Numerical readings are not available for these sources.

[b]Screening values obtained at the source surface with a J.W. Bacharach "TLV Sniffer" calibrated with n-hexane.

TABLE 4. NUMBER OF SOURCES SCREENING ABOVE 200 P.P.M.V.[a]

Source Type	Total Number Screened	Number Screened >200 p.p.m.[a]	Percent Screened >200 p.p.m.[a]
Valves	2249	624	27.7
Flanges	2100	45	2.1
Pump Seals	793	388	48.9
Compressors	175	133	76.0
Drains	254	29	11.4
Relief Valves[b]	101	31	30.7

[a]Screening values obtained at the source surface with a J. W. Bacharach "TLV Sniffer" calibrated with n-hexane.

[b]Venting directly to the atmosphere.

TABLE 5. RELATIVE EMISSION FACTORS FOR PROCESS STREAM GROUPS

Stream Type	Number Screened	Number Screened >200 p.p.m.[a]	Percent Screened >200 p.p.m.[a]	Normalized Emission Factor, wt./time
Valves				
Gas/Vapor Streams	682	204	29.9	1.00
Light Ends/ , Two-Phase Streams	1020	371	37.0	0.33
Kerosene and Heavier Streams	520	37	7.1	0.03
Pump Seals				
Light Ends/ Two-Phase Streams	478	304	63.6	1.00
Kerosene and Heavier Streams	295	67	22.7	0.13

[a]Screening values obtained at the source surface with a J. W. Bacharach "TLV Sniffer" calibrated with n-hexane.

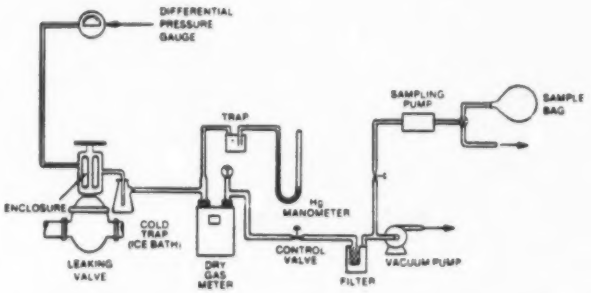

Fig. 1. Sampling train for baggable sources of hydrocarbon emissions.

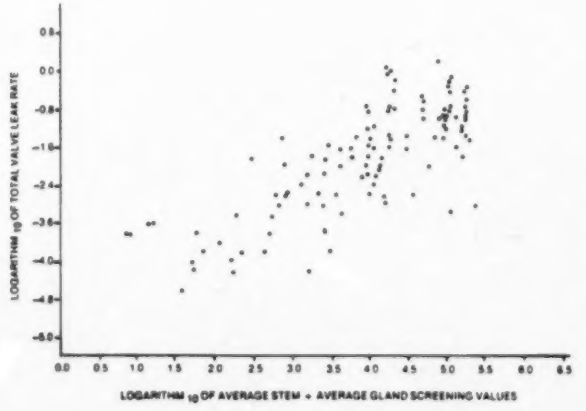

Fig. 2. Leak rates of valves as a function of screening values.

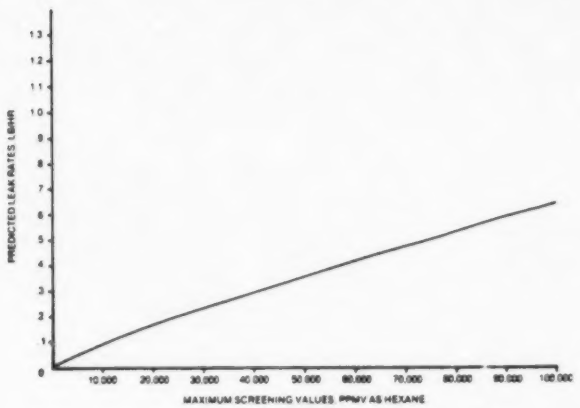

Fig. 3. Predicted leak rates as a function of maximum screening values.

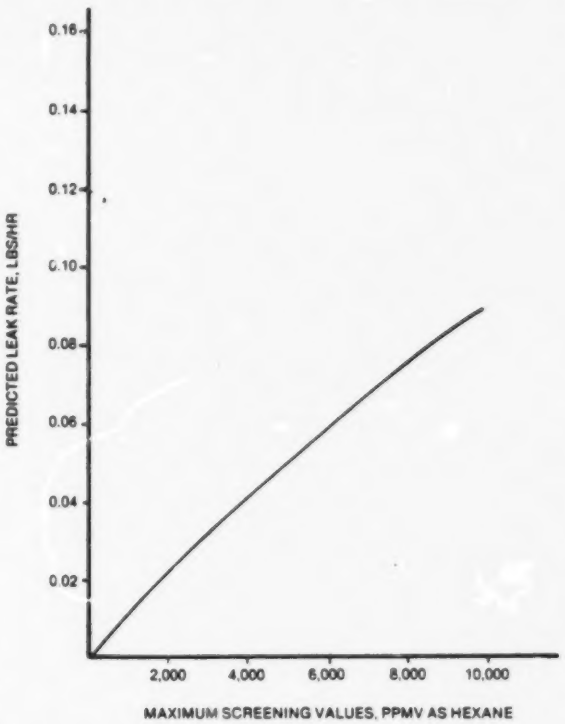

Fig. 4. Predicted leak rates as a function of maximum screening values—low range.